Production of nano-structured mouldings and coatings

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Abstract of **DE19719948**

Production of nano-structurised mouldings and coatings comprises: (a) preparing a fluid composition containing nano-scale inorganic solidly particles (I) with polymerisable and / or polycondensable organic groups on the surface; (b1) placing the composition in a mould or (b2) applying it to a substrate; and (c) polymerisation and / or polycondensation of the surface groups of (I) to form a cured moulding or coating. So claimed are nanostructurised mouldings and coatings produced in this way.

Description of **DE19719948**

The present invention concerns nanostrukturierte form bodies and layers as well as procedures to their production. In particular the present invention concerns nanostrukturierte form bodies and layers which are produced with the help of a wet-chemical procedure.

Nanostrukturierte materials are already known since longer time. They are produced as a rule by the fact that one condenses nanoskalige particles with diameters in the lower nanometer area by a suitable procedure (see e.g. H. Planing hull, Nanocrystalline of material, Pergamon Pressing, Oxford, in 1989). This mostly happens under high pressure. On this occasion, one uses the high diffusion rates in the outlying districts of the nanoskaligen particles and under effect of pressure (and under circumstances of concurrent effect of raised temperatures) a compression takes place to thick bodies. Suitable wet-chemical procedures, as for example the Sol gel process, lead as a rule to porous gels, because by the high surface activity of the particles, indeed, a connection the same takes place, however, thick lining up of the particles and filling the gusset does not occur. About such procedures made materials are uniform, i.e. they dispose of interface phases whose composition does not differ (substantially) from that of the particle phase (the gas phase of the surroundings can be present merely, in addition).

Now it was found astonishing-wise that when the nanoskaligen particles with polymerisierbaren and/or polycondenseable organic surface groups are provided and these surface groups

polymerisiert and/or are polycondensed on wet-chemical way nanostrukturierte material systems are accessible, up to now made on way on dry to the systems equally or even consider are. In particular highly clear materials are also accessible on this way, because the correlation lengths for the Rayleigh dispersion are not reached by the low distances of the particles to each other (one to a few nm).

The object of the present invention is therefore a procedure to the production of nanostrukturierten form bodies and layers which encloses the following steps:

a) Supply of a nanoskalige inorganic solid particle with polymerisierbaren and/or polycondenseable organic surface groups containing flowable mass;

b1) Introduce to the mass of step a) in a form; or
b2) application of the mass of step a) on a substrate

c) Polymerisation and/or polycondensation of the organic surface groups of the inorganic solid particles under education of a hardened form body or a hardened layer.

Mainly joins the above step c) a thermal aftercare, mainly at a temperature in the area of from 60 to 150 C DEG, in special from 80 to 130 C DEG, the hardened form body or the hardened layer.

Alternatively or, in addition, in addition a (other) thermal compression of the form body or the layer can occur at a temperature of least 250 C DEG, mainly at least 400 C DEG, and in particular at least 500 C DEG. In case of a layer on a substrate this thermal compression can be carried out of course only if the substrate material to such high temperatures can stand firm without interference as this is the case, e.g., with glass and many metals or alloys (however, also to some plastics).

In some cases it can also be an advantage to carry out a (other) thermal compression at temperatures in the area of from 800 to 1500 C DEG, mainly from 1000 to 1400 C DEG.

In the present description and in hanging claims those should not be meant under " nanoskaligen inorganic solid particles " by a middle particle size (a middle particle diameter) from more than 200 nm, mainly no more than 100 nm, and in particular no more than 70 nm. An especially preferential particle dimensions area lies with from 5 to 50 nm.

The nanoskaligen inorganic solid particles can exist of any materials, nevertheless, mainly they exist of metals and in particular of metal connections as for example to oxide like ZnO, CdO, SiO2, TiO2, ZrO2, CeO2, SnO2, Al2O3, In2O3, La2O3, Fe2O3, Cu2O, Ta2O5, Nb2O5, V2O5, MoO3 or WO3; Chalkogeniden as for example to sulphides (e.g., CdS, ZnS, PbS and Ag2S), Seleniden (e.g., gases, CdSe and ZnSe) and Telluriden (e.g., ZnTe or CdTe), Halogeniden like AgCl, AgBr, AgI, CuCl, CuBr, CdI2 and PbI2; Carbiden like CdC2 or Sic; to arsenide like AlAs, GaAs and GeAs; Antimoniden like InSb; Nitriden like BN, AlN, Si3N4 and Ti3N4; Phosphiden like GaP, InP, Zn3P2 and Cd3P2; to phosphates, silicates, Zirkonaten, Aluminaten, Stannaten and the suitable mixing oxide (e.g., such with Perowskitstruktur like BaTiO3 and PbTiO3).

Preferentially it concerns with in step a) of the erfindungsgemässen procedure used nanoskaligen inorganic solid particles such of oxide to sulphides, Seleniden and Telluriden of metals and mixtures the same. Erfindungsgemäss especially are preferred nanoskalige particles by SiO2, TiO2, ZrO2, ZnO, Ta2O5, SnO2 and Al2O3 as well as mixtures the same.

Because the erfindungsgemäss applicable nanoskaligen particles cover a wide area of Brechzahlen, can be put by suitable choice of these nanoskaligen particles the Brechzahl of a form body or a layer in comfortable way on the desired value.

The production of the erfindungsgemäss used nanoskaligen solid particles can occur in usual way, e.g., by Flammpyrolyse, plasma procedure Gas phases condensation procedure, colloid technologies, Präzipitationsverfahren, Sol-gel processes, controlled Nukleations-and growth processes, MOCVD procedures and (mike) emulsion-hopeless. These procedures are described in the literature in detail. In particular, e.g., metals can be pulled up (for example, after the reduction of the Fällungsverfahren), ceramic oxidische systems (by Präzipitation from solution), but also salt-like or Mehrkomponentensysteme. Solid-state systems also count to the salt-like or Mehrkomponentensystemen.

The production with polymerisierbaren and/or polycondenseable organic surface groups of provided nanoskaligen inorganic solid particles which are used erfindungsgemäss can be carried out in principle on two different ways, namely, on the one hand, by surface modification of already made nanoskaligen inorganic solid particles and on the other hand by production of these inorganic nanoskaligen solid particles under use of one or several connections which dispose of such polymerisierbare and/or polycondenseable groupings. These both ways are explained further below and in the examples closer.

With organic polymerisierbaren and/or polycondenseable surface groups it can concern any groups known to the expert which are accessible radikalischen, kationischen or anionischen, thermal or photo-chemical Polymerisation or a thermal or photo-chemical polycondensation (if necessary in presence of a suitable initiator or catalyst). Erfindungsgemäss are preferred surface groups which dispose of a (Meth) acrylic, Allyl-, vinyl or Epoxygruppe and (Meth) acrylic and Epoxygruppen are especially preferred. With the groups polycapable of condensation would be to be called, above all, Hydroxy-, Carboxy-and amino groups with whose help Ether-, Ester-and Amidbindungen can be received between the nanoskaligen particles.

Erfindungsgemäss is also preferred that in the surfaces of the nanoskaligen particles to the available organic groupings which enclose polymerisierbaren and/or polycondenseable groups a relatively low molecular weight show. In particular the molecular weight of the (purely organic) groupings 300 and mainly 200 should exceed, especially does not prefer 150. This does not exclude of course a clearly higher molecular weight of the connections enclosing these groupings (molecules).

As already on top mentioned the polycondenseable surface groups can be provided in principle on two ways. If a surface modification is already carried out of made nanoskaliger particles, everything are suited for this purpose (mainly down molecular) connections which dispose, on the one hand, of one or several groups which react with on the surface of the nanoskaligen solid particles to available (functional) groups (as for example oh-groups in case of from oxide) or can at least wechselwirken and show on the other hand at least one polycondenseable group. Therefore the suitable connections are able to, e.g. kovalente as well as Ionic (salt-like) or koordinative (Complicated) connections train to the surface of the nanoskaligen solid particles, while under the pure interaction exemplarily dipole dipole interaction, hydrogen bridges connections and from the Waals interaction would be to be called. The education from kovalenten and/or koordinativen connections is preferred. Concrete examples for for the surface modification of the nanoskaligen inorganic solid particles pullable up organic connections are, for example, unsaturated carboxylic acids like acrylic acid and Methacrylsäure, beta-Dicarbonyl-Verbindungen (e.g., beta-Diketone or beta-Carbonylcarbonsäuren) with polymerisierbaren double connections, ethylenisch unsaturated alcohols and amine, Epoxide and the like. Erfindungsgemäss especially prefers as such connections become in particular in the case of oxidischen particles - hydrolytisch condenseable Silane with at least (and mainly) to a not hydrolysierbaren rest which disposes of a polymerisierbare carbon carbon-double connection or an Epoxidring. Mainly such Silane show the general formula (I):
X-R <1>-SiR3 <2> (I)
in what X stands for CH2=CR <3>-COO, CH2=CH or Glycidyloxy, R <3> hydrogen or methyl explains, R <1> a bivalent hydrocarbon rest with from 1 to 10, mainly to from 1 to 6 carbon atoms

is which contains if necessary one or several Heteroatomgruppierungen (e.g., O, S., NH) which separate neighbouring carbon atoms of each other, and the rests R <2>, are same or passed away of each other, from Alkoxy-, Aryloxy-, Acyloxy-and Alkylcarbonylgruppen as well as halogen atoms (in particular fa, centilitre and/or Br) are selected.

Mainly the groups R <2> are identical and well-chosen from halogen atoms C1-4-Alkoxygrnppen (e.g., Methoxy, Ethoxy, n-Propoxy, i-Propoxy and Butoxy), C6-10-Aryloxygruppen (e.g., Phenoxy), C1-4-Acyloxygruppen (e.g., Acetoxy and Propionyloxy) and C2-10-Alkylcarbonylgruppen (e.g., Acetyl).

Especially preferential rests R <2> are C1-4-Alkoxygruppen and in particular Methoxy and Ethoxy.

With the rest R <1> it concerns mainly an Alkylengruppe, in particular around such with from 1 to 6 carbon atoms, as for example Ethylen, Propylen, Butylen and Hexylen. If X stands for CH2=CH, signifies R <1> mainly Methylen and can signify in this case also a bare connection.

Mainly shows X CH2=CR <3>-COO and R <3> mainly CH3 is) or Glycidyloxy. Especially preferential Silane of the general formula (I) (Meth) acryloyloxyalkyltrialkoxysilane as for example 3-Methacryloyloxypropyltri (m) ethoxysilan and Glycidyloxyalkyltrialkoxysilane as for example 3-Glycidyloxypropyltri (m) ethoxysilan are appropriate.

If the production of the nanoskaligen inorganic solid particles already occurs under use of one or several connections which dispose of polycondenseable groups, can be seen by an additional surface modification (although this is possible of course as an additional measure).

During situ production of nanoskaligen inorganic solid particles with polycondenseable surface groups would be explained in the following at the example by SiO2 particle. For this purpose the SiO2 particles can be produced, e.g., after the Sol gel process under use at least of one hydrolytisch polycondenseable Silans with at least one polycondenseable group. As such Silane, for example, the Silane described already on top of the general formula (I) are suited. These Silane become mainly either only or in combination with a suitable Silan of the general formula (II)
SiR4 <2> (II)
in what R <2> the meaning given on top shows, used. Preferential Silane of the above general formula (II) are Tetramethoxysilan and Tetraethoxysilan.

Of course it is also possible, additional or alternatively for the Silanen of the general formula (II) other Silane to start, e.g., those which dispose of a (nichthydrolysierbare) hydrocarbon group without any functional group, as for example methyl or Phenyltrialkoxysilane. In particular then if slightly to be cleaned (easily to clean) surface of the form body or the layer is wished, it can be recommendable to use a certain amount (e.g., up to 60 and in particular up to 50 Molprozent on the base all used Silane) Silane with fluorine-containing (not hydrolysierbaren) rests, in particular to hydrocarbon leftovers beside the Silanen of the general formula (I) and if necessary the general formula (II). Especially are preferred, on this occasion, Silane of the above formula (I) in which R <2> are defined as on top, show R <1> an Ethylengruppe and X stands for a Perfluoralkylgruppe with from 2 to 12, mainly from 4 to 8, carbon atoms. Other Silane applicable for this purpose are, e.g., those with (by) fluoridated Aryl-(in particular Phenyl) trench. Of course such fluoridated Silane can also make for the surface modification from already to nanoskaligen inorganic solid particles are used.

In step a) of the erfindungsgemässen procedure used material is in form of a still flowable mass (suspension). The liquid component of this mass sits down, for example, of water and/or (mainly with water mixable) organic solvent and/or connections which were used in the course of the production of the nanoskaligen particles or their surface modification or were generated (e.g., to alcohols in case of by Alkoxysilanen), together. Suitable organic solvents are, for example, alcohols, Ether, Ketone, Ester, Amide and the like. A (additional) component of the flowable mass can be, for example, however, also at least one monomere or oligomere species which dispose of

at least one group which react with in the surface of the nanoskaligen particles to available polycondenseable groups (polymerisieren or polycondense) is able to. As such species are, e.g. Monomers with a polymerisierbaren double connection as for example Acrylsäureester, Methacrylsäureester, styrene, vinyl acetate and vinylchloride called. As (prefers used) monomere connections with more than one polymerisierbaren connection are called in particular such of the general formula (III):
(CH2=CR <3>-COZ-) n-A (III)
in what
n = 2, 3 or 4, mainly 2 or 3 and in particular 2;
Z = O or NH, mainly O
R <3> = H, CH3;
A = the n valued hydrocarbon rest with from 2 to 30, in particular to from 2 to 20 carbon atoms which can show one or several Heteroatomgruppierungen which are in each case between two neighbouring carbon atoms (examples of such Heteroatomgruppierungen are O, S., NH, NO. (R = a hydrocarbon rest), mainly O).

Further the hydrocarbon rest A one or several Substituenten which are mainly selected from halogen (in particular fa, centilitre and/or Br), Alkoxy (in particular C1-4Alkoxy), Hydroxy, if necessary to substituted Amino, NO2, OCOR <5>, COR <5> (R <can carry 5> = C1-6-Alkyl or Phenyl). Nevertheless, mainly the rest A is substituted unsubstituted or with halogen and/or Hydroxy.

In an especially preferential execution form of the present invention is derived A from aliphatischen Diol, to an Alkylenglycol, a Polyalkylenglycol or if necessary alkoxylierten (e.g., ethoxylierten) Bisphenol (e.g., Bisphenol A). In this connection are preferential Alkylenglycole Ethylenglycol, Propylenglycol and Butylenglycol, in particular Ethylenglycol.

Other applicable connections with more than one double connection are, for example, Allyl (meth) acrylat, Divinylbenzol and Diallylphthalat. Also, for example, a connection with 2 or more Epoxygruppen can be used (in the case of the use of Epoxid containing surface groups), e.g., Bisphenol A-diglycidylether or also a (oligomeres) precondensate of an Epoxidgruppenhaltigen hydrolysierbaren Silans (e.g., Glycidoxypropyltrimethoxysilan).

If additional monomere connections with polycondenseable groups are used, their interest puts out % mainly no more than 20 weights, in particular no more than 15 and especially prefers no more than 10 weights % of the whole solid salary of the flowable mass of step a).

In step b) of the erfindungsgemässen procedure the flowable mass is introduced by step a) either in a suitable form to produce a form body, or on a desired substrate angry to coat the substrate all or part. The coating procedures suitable for this purpose are the customary ones and the expert confessed. Examples for this are a diving, spraying, Rakeln, to pranks, brushes, skidding etc.

Before the bringing in in the form or to the application on the substrate the flowable mass can be put, for example, by addition of solvent or vaporisation of brief components (in particular already to available solvent) on a suitable viscosity.

Substrates from any materials in particular of plastics, metal and glass are suited for the coating with the flowable mass of step a) of the erfindungsgemässen procedure. These substrate materials can be submitted before the Aufbringung of the flowable mass if necessary to a surface treatment (e.g., Entfettung, roughening, Corona-unloading, treatment with a Primer etc.) . In particular in case of the coating of plastic substrates a suitable liability can be provided by addition suitable monomeren polymerisierbaren connection. Under the erfindungsgemäss coatable metal substrates are as examples metals as for example aluminium, copper, zinc, nickel and chrome and alloys as (Nobly) stole, brass and bronze called. Suitable plastic substrates are, for example, those from Polycarbonat, polyester, polyamides, polystyrene, Poly (meth) acrylaten (e.g., Polymethylmethacrylat) and PVC.

In step c) of the erfindungsgemässen procedure a Polymerisation and/or polycondensation of the polycondenseable surface groups of the nanoskaligen organic solid particles (and if necessary the polycondenseable groups is carried out, in addition, used monomeren or oligomeren species). This Polymerisation/polycondensation can be carried out in the way familiar to the expert. Mainly a such Polymerisation/polycondensation occurs in presence of a suitable catalyst or starter (initiator) which is added to the flowable mass by step a) at the latest immediately before their bringing in in the form or application on the substrate.

As starters / starter systems all familiar ones and the expert known starter / start systems are possible, including radikalischer photo starter, radikalischer thermo starter, kationischer photo starter, kationischer thermo starter and any combinations the same.

Concrete examples of applicable radikalische photo starters are Irgacure a TM 184 (1-Hydroxycyclohexylphenylketon), Irgacure TM 500 (1-Hydroxycyclohexylphenylketon, Benzophenon) and other photo initiators available from the company Ciba-Geigy of the Irgacure Tm type; Darocur TM 1173, 1116, 1398, 1174 and 1020 (available from the company Merck); Benzophenon, 2-Chlorthioxanthon, 2-Methylthioxanthon, 2-Isopropylthioxanthon, Benzoin, 4.4 '-Dimethoxybenzoin, Benzoinethylether, Benzoinisopropylether, Benzildimethylketal, 1,1.1-Trichloracetophenon, Diethoxyacetophenon and Dibenzosuberon.

Examples of radikalische thermo starters are and a. organic Peroxide in the form of Diacylperoxiden, Peroxydicarbonaten, to Alkylperestern, Alkylperoxiden, Perketalen Ketonperoxiden and Alkylhydroperoxiden as well as Azo connections. As concrete examples would be to be called here in particular Dibenzoylperoxid, tert-Butylperbenzoat and Azobisisobutyronitril.

An example of a kationischen photo starter is Cyracure a TM UVI-6974, while a preferential kationischer thermo starter 1-Methylimidazol is.

These starters are covered in the usual amounts known to the expert (mainly 0,01-1 Gew.-%, in particular 0,1-0,5 Gew.-%, on the whole solid salary of the flowable mass are used by step a)).

The Polymerisation/polycondensation of step c) of the erfindungsgemässen procedure occurs mainly thermally or by radiotherapy (in particular with ultraviolet light). Especially a photo-chemical Polymerisation/polycondensation or a combination of thermal and photo-chemical Polymerisation/polycondensation is preferred.

Can lead the way of the Polymerisation/polycondensation a distance of other brief, nicht-polymerisierbaren/not-polykondensierbaren connections from in the form or on the substrate located mass. However, this distance of brief components can occur also or, in addition, on the step of the Polymerisation/polycondensation or afterwards.

In the following a typical erfindungsgemässes procedure which can lead to clear form bodies should be outlined exemplarily and the given value areas and approaches own general validity regardless of the specifically used materials.

Nanoskalige particles from, for example, SiO2, TiO2, ZrO2 or other oxidischen or sulfidischen materials (particle size from 30 to 100 nm, mainly from 40 to 70 nm) are covered in a solvent (for example, in a low alcohol like methanol, Ethanol, Propanol) in a concentration of from 1 to 20 Gew.-%, mainly from 5 to 15 Gew.-%, dispergiert and with surfaces modification means with polycondenseable groups in an amount from mainly from 2 to 25 Gew.-%, in particular from 4 to 15 Gew.-% (to the whole solid salary), moved. The surface modification Can touch in the case of the use of for example Silanen by mehrstündiges with ambient temperature are carried out. Afterwards if necessary is able to still monomeres or oligomeres material with polycondenseable groups, with the surfaces modification means or. to the surface groups it is compatible, in an

amount from, for example, up to 20 Gew.-%, mainly from 4 to 15 Gew.-%, (covered on the whole solid salary) are added. After addition of one or several suitable starters (in each case in an amount from, for example, from 0.01 to 1 Gew.-% mainly from 0.1 to 0.5 Gew.-%, covered to the whole solid salary) the solvent is partially removed (mainly to from 50 to 98, in particular from 75 to 95%). Then the still flowable mass is given in the desired form what the distance of the remaining solvent joins. Afterwards the first Härtung is carried out. For the decrease of the response times mainly a Photopolymerisation is used; any sources of light, in particular ultraviolet light emitting springs, are applicable, on this occasion (e.g., mercury steam lamps, xenon lamps, laser light etc.) . "Rapid Prototyping" the age-hardening with laser light permits an application for so-called. After a thermal Nachhärtung to the other compression of the structure (e.g., 0,5-4 hours with from 70 to 150 C DEG, mainly 1-2 hours with from 80 to 100 DEG C) a green body will receive. This green body can be heated, e.g., within from 2 to 10 hours, mainly from 3 to 5 hours, on a temperature by e.g. 500 C DEG and be held, for example, from 2 to 10 hours (mainly 3-5 hours) at this temperature. This step leads in most cases to the entire loss of the organic (carboniferous) groupings in the form body. Then to the final compression the form body can be heated within e.g. from 2 to 10 hours (mainly 3-5 hours) on a temperature by for example 1400 C DEG and be held, for example, from 1 to 5 hours (mainly 2-3 hours) at this temperature. Thus a colorless, clear, purely inorganic form body can be received.

The layer production can become, for example, so gone forward that hydrolysierbare Silane with polycondenseable groups in a concentration from mainly no more than 100 Gew.-%, in particular no more than 75 Gew.-% (covered to Nanopartikel), to soles with, for example, oxidischen or sulfidischen Nanopartikeln are given. After viscosity setting by addition or distance of solvent (e.g., alcohol) and after addition of a photo initiator (e.g., in a concentration of 5 Gew.-% covered to the used Silan) an age-hardening of the layer on the elective substrate with mainly ultraviolet light leads to clear and homogeneous layers free of tear. A thermal aftercare with for example from 60 to 100 C DEG leads as a rule to a significant improvement of the layer qualities, nevertheless, is not indispensable. The so made layers show a good wear permanence. Because with this procedure the thermal aftercare is practicable at relatively low temperatures, substrates with low thermal stability can be also used easily. As already on top mentioned, insists by variation of the amount and kind of the used Silans and by the addition of an additional organic monomer (Methacrylate, Acrylate etc.) in low concentrations (for example, <5 Gew.-%) the possibility on adapting the custody qualities of the layer to the substrate so that, e.g., glass and plastics can be equally coated. Further the couse of the fluoridated Silane mentioned on top leads by the surface modification to easy-to-clean-Schichten on the suitable substrates.

The following examples serve the other explanation of the present invention.

Example 1

Production of a clear organikfreien SiO2-form body

SiO2 particles (OX-50, primary particle size 40 nm) become in a concentration of 10 Gew.-% under touching and ultrasound about 30 minutes in Isopropanol dispergiert. On it 3-Methacryloxypropyltrimethoxysilan (MPTS) becomes in an amount from 6 Gew.-%, covered to the SiO2 content, added slowly under stirring. A Silanisierung of the SiO2 particles is reached by 3-hour stirring with 50 C DEG. 6 are covered to it Gew.-% (on the whole solid salary) Tetraethylenglycoldimethacrylat (TEGDMA) allowedly and it is stirred other 15 minutes. In the end, as a photo starter for the UV-Polymerisation 2 are added Mol-% Irgacure TM 184 (Ciba-Geigy) per Mol double connection. On it the solvent becomes under vacuum partially abdestilliert (entire Abdestillieren of the alcohol leads to the gel education, so that no more flowable or pouring-capable suspension can be received). The so preserved suspension can serve directly for the

production of Bulkmaterialien by Photopolymerisation.

Moreover the SiO2/MPTS/TEGDMA system is poured in a Polyethylen-form body. To the degassing this is treated viskose Sol again under vacuum (100 mbar) during 1 hour with 25 C DEG. For the interlinking of the organic interest an UV/Ir combination dryer (company Beltron) is used. The achievement of the mercury steam lamps amounts in each case to 400 mW/m <2>. The complete Photopolymerisation of a Bulks of 5 mm of thickness is reached by a radiotherapy amount from 240 J/cm <2>. After the Photopolymerisation a form-stable body is. A drying free of tear photopolymerisierten Bulks is carried out within one hours by stove treatment with 80 C DEG. Thereby one receives a binding agent-containing SiO2-form body free of solvent which corresponds to a ceramic green body. To burn out the remaining organic interest, the temperature of the stove is raised within 3 hours by 80 C DEG on 500 C DEG on which the last-called temperature will maintain another 3 hours. Thus one receives a porous SiO2-Bulk which, how from IR-spektroskopischen investigations can be closed, is free of organic groups. In the end, the temperature is raised within 3 hours by 500 C DEG on 1400 C DEG and then the last-called temperature is held still during 2 hours. In the end, thus one receives a clear form body.

Example 2

Production of an organikfreien clear ZrO2-form body

Nanoskalige zircon oxide particles (" TOSOH-Zirnonia of TZ-8Y " by a primary particle size of 90 nm) become under touching and ultrasound in Isopropanol dispergiert. For the surface modification are covered to the suspension 3.2 Gew.-% (to the ZrO2 content) MPTS under stirring are added. After 3-hour stirring with 50 C DEG a Silanisierung of the ZrO2 particles is reached. 3.2 are covered to it Gew.-% (on the ZrO2 content) TEGDMA allowedly and it is stirred other 15 minutes with 20 C DEG. Then as photo starters 3 are added Mol-% Irgacure TM 184 per Mol double connection. A partial distance of the solvent joins this under vacuum. The so preserved, still flowable suspension serves directly for the production of Bulkmaterialien by Photopolymerisation. To receive a form body with a thickness from 5 mms, an achievement of 350 J/cm <2> is used.

A drying free of tear photopolymerisierten Bulks is reached within 30 minutes by stove treatment of the photopolymerisierten form body with 80 C DEG. Thereby one receives a binding agent-containing ZrO2-Bulk free of solvent which corresponds to a ceramic green body. To burn out the remaining carbon interest, the temperature of the stove is raised within 3 hours by 80 C DEG on 450 C DEG and is held 3 hours at the last-called temperature. One receives thus a porous ZrO2-Bulk which is freely from organic groups. In the end, the temperature is raised within 3 hours by 450 C DEG on 1400 C DEG and is held 4 hours with the last-called value. The sintered form body preserved thereby is transluzent to opaque.

Example 3

Synthesis of a Sols to the production of layers with high Brechwert

86,861 gs TiO2-Sol (3.5 Gew.-% TiO2 in Isopropanol; particle size: 5 nm) are moved with 1,989 gs Phosphorsäuretributylester and are stirred 1 hour. Afterwards the Sol is moved with 100 C DEG drop by drop with a solution of 1.2 gs distilled gamma-Glycidyloxypropyltrimethoxysilan

(GPTS) into 100 gs 2-Isopropoxyethanol.

After 1-hour stirring the beginning on ambient temperature is cooled and it are added 0,8775 gs hydrolysiertes GPTS (made by moving of 23.63 gs distilled GPTS with 2.70 gs 0.1 N to HCl and 24-hour touching as well as next Abdestillieren of down molecular reaction products with 3 mbar). After 15-minute stirring the beginning is distilled under vacuum (3 mbar) and afterwards is diluted with 120 gs 2-Isopropoxyethanol. Thus becomes a clear, agglomeratfreies Sol receive.

Example 4

Synthesis of a Sols to the production of layers with low Brechwert

A mixture of 23.63 gs GPTS (distills) and 12.45 gs Tetraethoxysilan (TEOS) it is moved for the purpose of Hydrolyse and condensation with 2.88 gs 0.1 N HCl. Afterwards the resultant reaction mixture is stirred 24 hours with 20 C DEG and then is submitted to a vacuum distillation (with 3 mbar) for the purpose of distance of down molecular components. Finally the remained reaction product with 50 gs Isopropoxyethanol is diluted as a solvent.

Example 5

Synthesis of a Sols to the production of layers with low Brechwert and, more in addition, easy-to-clean-Funktion

These become 26.63 gs distilled GPTS with 8.30 gs TEOS and 0.11 gs of 1H, 1H, 2H, 2H--Perfluoroctyltriethoxysilan (FTS) 15 minutes under stirring mixed. The resultant Sol becomes with 20 C DEG during 4 hours with 4.5 gs 0.1 N HCl under stirring hydrolysiert and is condensed. On it 52.10 gs Isopropoxyethanol and 0.53 gs of phosphorus acid are added and it is stirred other 2 hours with 20 C DEG.

Example 6

Production of a layer with the Sol from example 3 on glass

The Sol from example 3 is moved with 0.08 gs Cyracure TM UVI-6974 (Ciba-Geigy) and 0.02 gs 1-Methylimidazol. After intensive stirring the mixture is filtered and then is applicable as a coating varnish. Windowpanes (10 cm x 10 cm x 2 mms) are cleaned before the coating with 2-Propanol and are dried in air.

The coating varnish is raised by catapult coating defined on the substrate. The layer thickness is steered about the rotating speed of the substrate.

For the age-hardening of the layer an UV/Ir combination dryer (from company Beltron) is used. The used device orders more than two mercury steam lamps to the radiotherapy with ultraviolet light, an Ir emitter about whose achievement the surface temperature can be regulated, and a run

tape on which the substrates can be led under the UV/Ir emitter at defined speed. The achievement of the mercury steam lamps amounts in each case to 400 mW/cm <2>.

The Ir emitter is put on 120 C DEG, the tape run speed amounts to 2.6 m / min. and the coated substrates become driven past a total of three times with these settings.

The last step of the Aushärtens exists of a 15-minute thermal aftercare with 120 C DEG in an Umlufttrockenschrank.

Example 7

Production of a layer with the Sol from example 3 on Polycarbonat (PC)

With the coating material from example 3 become Polycarbonat discs (10 cm x 10 cm x 2 mms; pretreatment like in example 6) after the procedure of example 6 coatedly and hardened. Differences: the Ir emitter is put on 100 C DEG and the last step of the Aushärtens exists of a 30-minute thermal aftercare with 100 C DEG in an Umlufttrockenschrank.

Example 8

Production of a layer with the Sol from example 3 on Polymethylmethacrylat (PMMA)

With the coating material from example 3 become Polymethylmethacrylat-discs (10 cm x 10 cm x 2 mms; pretreatment like in example 6) after the procedure of example 6 coatedly and hardened: Differences: no Ir radiotherapy and the last step of the Aushärtens exists of a 60-minute thermal aftercare with 80 C DEG in an Umlufttrockenschrank.

Example 9

Production of a layer with the Sol from example 4 on PC

The coating material from example 4 is moved with 0.72 gs Cyracure TM UVI-6974, 0.36 gs 1-Methylimidazol and 10 gs of a 0.02-weight-percent Aluminiumtributoxyethanolat solution into 2-Isopropoxyethanol and is intensely mixed. The necessary thinner is reached by addition of 50 gs 2-Isopropoxyethanol. With this coating material Polycarbonat discs (see example 7) are coated after the procedure by example 7 and are hardened. Differences: the substrates become a 4-spot with a tape run speed of 2 m / min. driven past and the last step of the Aushärtens exists of a 60--minute thermal aftercare with 100 C DEG in an Umlufttrockenschrank.

Example 10

Production of a layer with the Sol from example 4 on PMMA

It will proceed like in example 9, however, without use of the Ir emitter. The last step of the Aushärtens exists of a 60-minute thermal aftercare with 70 C DEG in an Umlufttrockenschrank.

Example 11

Production of a layer with the Sol from example 5 on PC

The coating material according to example 5 is provided according to example 8 with initiators and is hardened after in example to 8 described procedures.

Qualities in the examples to from 6 to 11 made layers

Investigation methods
Brechwert: Ellipsometrisch
Transmission (550 nm): Spektroskopisch (one-sided coating of the substrates)
Reflexion (550 nm): Spektroskopisch (uncoated back of the substrates blackened)
Liability (layer on substrate): Grid cut and adhesive tape test according to German Institute for Standardization 53151 and German Institute for Standardization 58196.

The so preserved values are summarised into the following table.

EMI19.1

Claims of **DE19719948**

1. Procedures to the production of nanostrukturierten form bodies and layers extensively the following steps:

a) Supply of a nanoskalige inorganic solid particle with polymerisierbaren and/or polycondenseable organic surface groups containing flowable mass

b1) bringing in of the mass of step a) in a form; or
b2) application of the mass of step a) on a substrate; and

c) Polymerisation and/or polycondensation of the surface groups of the solid particles under education of a hardened form body or a hardened layer.

2. Procedures after claim 1, thereby marked that it encloses a thermal aftercare, mainly at a temperature in the area of from 60 to 150 C DEG, the form body or the layer of step c) as an

additional step.

3. Procedures after any of the claims 1 and 2, thereby marked that it encloses a thermal compression of the form body or the layer at a temperature of at least 250 C DEG, mainly at least 400 C DEG as an additional step.

4. Procedures after any of the claims from 1 to 3, thereby marked that the nanoskaligen particles are selected from such of metal connections, in particular to oxide, sulphides, Seleniden and Telluriden of metals and mixtures the same.

5. Procedures after any of the claims from 1 to 4, thereby marked that the nanoskaligen particles are selected from such of SiO_2, TiO_2, ZrO_2, ZnO, Ta_2O_5, SnO_2 and Al_2O_3 and mixtures the same.

6. Procedures after any of the claims from 1 to 5, thereby marked that polymerisierbaren and/or polycondenseable surface groups are selected from organic rests which dispose of a (Meth) acrylic, vinyl, Allyl-or Epoxygruppe.

7. Procedures after any of the claims from 1 to 6, thereby marked that in step a) to used solid particles were produced by surface modification of nanoskaligen solid particles with the suitable surface groups.

8. Procedures after any of the claims from 1 to 6, thereby marked that are produced in step a) to used solid particles under use at least of one connection with suitable polycondenseable groups.

9. Procedures after any of the claims from 1 to 8, thereby marked that the production of the inorganic solid particles occurs after the Sol gel procedure.

10. Procedure shows the inorganic solid particles of step a), in addition, fluoridated surface groups, mainly such in what Rf a Perfluoralkylrest with from 2 to 12 carbon atoms after any of the claims from 1 to 9, with it marked that, show.

11. Procedures after any of the claims from 1 to 10, thereby marked that step c) is not carried out in presence from to the solid particles engaged polymerisierbaren and/or polycondenseable monomeren or oligomeren species.

12. Procedures after any of the claims from 1 to 11, thereby marked that step c) is carried out in presence of a thermo starter and/or photo starter.

13. Procedures after any of the claims from 1 to 12, thereby marked that step c) a photo-chemical Polymerisation/polycondensation encloses.

14. Procedures after any of the claims from 1 to 13, thereby marked that it concerns with the substrate of step b2) such of plastic, metal or glass.

15. Nanostrukturierte form body, available after the procedure according to any of the claims from 1 to 14.

16. With a nanostrukturierten layer of provided substrate, available after the procedure according to any of the claims from 1 to 14.